

# PATENT ABSTRACTS OF JAPAN

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(21)Application number : 2000-111641 (71)Applicant : TORAY IND INC

(22)Date of filing : 13.04.2000 (72)Inventor : MATSUMURA NOBUO  
KAMIOKA TAKENORI

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(54) GLASS PASTE

(57)Abstract:

**PROBLEM TO BE SOLVED:** To solve such a problem which is caused when electronic parts are manufactured by the thick film printing method, that magnetic body powder and dielectric powder can not be sintered when the sintering is carried out at 1,000°C or lower temperature since a silver electrode low in resistance is used and magnetic permeability and dielectric constant are deteriorated when a large amount of glass is incorporated as a sintering auxiliary agent.

**SOLUTION:** This glass paste contains a binder resin and inorganic powder which contains at least one kind of powder selected from magnetic body powder and dielectric powder and glass powder having 400°C or higher to lower than 520°C softening point.

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## CLAIMS

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[Claim(s)]

[Claim 1]Inorganic powder, at least one sort of powder chosen from magnetic substance powder and dielectric powder as inorganic powder in a paste containing binder resin, and a paste in which softening temperature is characterized by containing not less than 400 \*\* the glass powder it is [ glass powder ] less than 520 \*\*.

[Claim 2]The paste according to claim 1, wherein magnetic substance powder is a ferrite.

[Claim 3]The paste according to claim 1, wherein magnetic substance powder is a ferrite of a nickel zinc system or a nickel zinc-copper system.

[Claim 4]Dielectric powder Barium titanate, strontium titanate, calcium zirconate, Titanic acid calcium, lead titanate, a lead wolframate, a lead wolframate, The paste according to claim 1 which are lead zincate, lead ferrate, magnesium acid lead, magnesium acid lead, lead niobate, nickel acid lead, lead zirconate, a compound perovskite system dielectric, and at least one sort of dielectric compounds chosen from a group of titanium oxide.

[Claim 5]The paste according to claim 1, wherein a ratio of glass powder to the inorganic powder whole quantity is less than [ more than 30vol%50vol% ].

[Claim 6]The paste according to claim 1, wherein binder resin is an acrylic copolymer.

[Claim 7]The paste according to claim 1 containing an azole compound.

[Claim 8]The paste according to claim 1, wherein mean particle diameter of glass powder is 0.5 micrometers or more less than 5 micrometers.

[Claim 9]The paste according to claim 1 whose mean particle diameter of inorganic powder other than glass powder is characterized [ the feature and / to carry out ] by 0.1-micrometer or more being less than 1 micrometer.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention is printed and calcinated on a ceramics board or a conductor, and relates to the inorganic powder distribution paste for forming a magnetic layer, a dielectric layer, etc.

[0002]

[Description of the Prior Art]The multi chip module carried in a personal computer and a PC card in recent years, A demand of a miniaturization, densification and highly-minute-izing, and high-reliability is increasing to electronic parts or ceramic multilayer substrates, such as a filter for high frequency of mobile transmitter dexterous ways, such as a chip-size package or a cellular phone, a chip inductor, and a multilayer ceramic capacitor. It is necessary to these demands to control the amplitude permeability and the dielectric constant of an insulating layer between conductor layers.

[0003]While forming a conductor layer and an insulation layer, there is thick film printing as law. This forms the paste containing inorganic powder and binder resin, such as the end of conducting powder, and glass powder, in desired thickness and shape by screen-stencil etc., makes inorganic powder sinter and forms a conductor film and glass membrane while carrying out decomposition volatilization of the binder resin by

calcinating at an elevated temperature. In thick film printing, it is easy to thicken a conductor film or to carry out the simultaneously form of the passive components, such as a resistor. In recent years, silver and copper of low resistance are used more often as a conductor. Since a conductive pattern will dissolve and shape will collapse if it calcinates exceeding the melting point of a conductor, to use silver and copper for a conductor, it is necessary to also calcinate an insulation layer at less than 1000 \*\*. Therefore, as an insulation layer when using silver as a conductor, the mixture of not conventional alumina (calcination temperature of not less than 1600 \*\*) but glass and the glass called crystallized glass, and ceramics is used.

[0004]

[Problem(s) to be Solved by the Invention]Now, as an inter-electrode dielectric layer of a capacitor, in order to raise the electric capacity of a capacitor, the ferroelectric represented by barium titanate etc. is used. It is desirable to use the magnetic body of a ferrite series for the material between layers for the improved efficiency of a coil component. However, since neither a ferrite nor barium titanate can be sintered at less than 1000 \*\*, it is difficult for it to use together with low resistance conductors, such as silver and copper. Although there was the method of lowering sintering temperature by mixing glass as a sintering aid, when it was going to sinter at less than 1000 \*\*, there was a problem which must mix glass so much therefore to which the performance as a magnetic body or a dielectric falls.

[0005]Including a magnetic body, dielectric powder, and glass, the purpose of this invention is to supply the paste in which calcination at less than 1000 \*\* is possible, though it has high amplitude permeability and dielectric constant.

[0006]

[Means for Solving the Problem]This inventions are inorganic powder, at least one sort of powder chosen from magnetic substance powder and dielectric powder as inorganic powder in a paste containing binder resin, and a paste in which softening temperature is characterized by containing not less than 400 \*\* the glass powder it is [ glass powder ] less than 520 \*\*.

[0007]

[Embodiment of the Invention]Although this invention is explained concretely below, this invention does not receive any restriction by these explanation.

[0008]This invention is a paste which contains magnetic substance powder, dielectric powder, and glass powder as inorganic powder, and though it has high amplitude permeability and dielectric constant, the paste which can be calcinated at less than 1000 \*\* is obtained.

[0009]As dielectric powder used by this invention, barium titanate, strontium titanate, Calcium zirconate, titan acid calcium, lead titanate, a lead wolframate, Although a lead wolframate, lead zincate, lead ferrate, magnesium acid lead, magnesium acid lead, lead niobate, nickel acid lead, lead zirconate, a compound perovskite system dielectric, titanium oxide, etc. are raised, it is not limited to these. Although each of these has a high dielectric constant, alone, they cannot be calcinated at the temperature below 1000 \*\*.

[0010]Ferrite powder is raised as magnetic substance powder used by this invention. Also in ferrite powder, soft ferrites, such as a nickel zinc system and a nickel zinc-copper system, are suitably used for a magnetic cell use. Alone, these magnetic substance powder cannot be calcinated at less than 1000 \*\* to the above-mentioned dielectric

powder and agitation, either.

[0011]As mean particle diameter of these dielectric powder and magnetic substance powder, D50 mean particle diameter is used and it is desirable that it is [ 0.1 micrometer or more ] less than 1 micrometer. It is very easy to condense the particles below 0.1 micrometer to a degree in a paste, and they reduce printing surface smoothness etc.

Again. If particles become a size of 1 micrometers or more, after sintering, it will be difficult to obtain a good film and a membranous electrical property will fall.

[0012]As glass powder used by this invention, the thing below not less than 400 \*\* and 520 \*\* has preferred softening temperature. It softens, before an organic component carries out decomposition volatilization to softening temperature being glass below 400 \*\* at the time of calcination, and an organic matter is wrapped in, and it becomes a cause by which an organic matter remains after calcination. In order for a degree of sintering to fall when softening temperature is not less than 520 \*\*, and the content of magnetic substance powder or dielectric powder is raised, performances, such as sufficient amplitude permeability and a dielectric constant, are not obtained.

[0013]Although there is borosilicic acid system glass which contains lead or bismuth as such low softening point glass, a bismuth system is more preferred when the material which contains lead from an environmental problem in recent years takes that regulation is progressing into consideration.

[0014]As mean particle diameter of glass powder, D50 mean particle diameter is used and it is desirable that it is [ 0.5 micrometer or more ] less than 5 micrometers. It is very easy to condense a glass particle with a mean particle diameter of less than 0.5 micrometer to a degree in a paste, and it reduces printing surface smoothness etc. Again. For the size of the grain child itself from which mean particle diameter becomes a size of not less than 5 micrometers, unevenness occurs in a printed film side and surface smoothness is reduced to it.

[0015]As a rate of a compounding ratio of glass powder, and other mineral constituents, i.e., a dielectric, and/or magnetic substance powder, the volume ratio of glass powder is used and less than [ more than 30vol%50vol% ] is preferred. Since it is a volume fraction of each ingredient, a volume ratio is important for determining the membranous amplitude permeability and dielectric constant of a complex component. Since it was difficult on the occasion of powdered combination to measure volume, after asking for the true specific gravity of the mineral constituent of glass and others practically, it is good for the following number (1) to determine the weight-mix ratio which should be carried out by calculation from a desirable volume compounding ratio.

[0016]When measuring the weight ratio of each ingredient by analysis from a paste presentation and asking for the volume compounding ratio of a glass component and other mineral constituents, it is good for the following number (2) to perform similarly.

[0017]

[Equation 1]

$$R_g = \frac{R_v \times G_d}{R_v \times G_d + (100 - R_v) \times 1_d} \times 100 \quad (1)$$

[0018]

[Equation 2]

$$R_v = \frac{R_g + G_d}{R_g + G_d + (100 - R_g) \times 1_d} \times 100 \quad (2)$$

[0019]It is here and is a weight-mix ratio (wt%) of Rg:glass.

Rv: The volume compounding ratio of glass (vol%)

Gd: True density (g/cm<sup>3</sup>) of glass

Id: True density (g/cm<sup>3</sup>) of mineral constituents other than glass.

[0020]It can use without being limited especially if it is the resin thing which is used as binder resin of a common calcination system paste as a binder resin component and which a pyrolysis and volatilization make prompt. There are cellulose type resin and acrylic resin as those examples. Ethyl cellulose is raised as cellulose type resin. Acrylic resin is a copolymer which contains an acrylic system monomer in a copolymerization ingredient at least, and with an acrylic system monomer. As a concrete example, methyl acrylate, ethyl acrylate, n-propylacrylate, Isopropyl acrylate, n-butyl acrylate, sec-butyl acrylate, Isobutyl acrylate, tert-butyl acrylate, n-pentyl acrylate, Allyl acrylate, benzyl acrylate, butoxy ethyl acrylate, Butoxytriethylene glycol acrylate, cyclohexyl acrylate, Dicyclopentanil acrylate, dicyclopentenylacrylate, 2-ethylhexyl acrylate, glycerol acrylate, glycidyl acrylate, Heptadecafluorodecyl acrylate, 2-hydroxyethyl acrylate, ISOBO nil acrylate, 2-hydroxypropyl acrylate, ISODEKI sill acrylate, Isooctyl acrylate, laurylacrylate, 2-methoxy ethyl acrylate, methoxy ethylene glycol acrylate, methoxy diethylene-glycol acrylate, octaphloropentyl acrylate, Phenoxy ethyl acrylate, stearylacrylate, triphloroethyl acrylate, Acrylamide, aminoethyl acrylate, phenyl acrylate, Acrylic system monomers, such as phenoxy ethyl acrylate, 1-naphthyl acrylate, 2-naphthyl acrylate, thiophenol acrylate, and benzyl mercaptan acrylate, the thing which replaced these acrylate with methacrylate, etc. are mentioned. It is alkyl acrylate or alkyl methacrylate, and that methyl methacrylate is included at least more preferably desirably, and the good polymer of pyrolysis nature can be obtained. Although it is usable as copolymerization ingredients other than an acrylic system monomer in all the compounds which have a carbon carbon double bond, Preferably Styrene, p-methylstyrene, o-methylstyrene, m-methylstyrene, Styrene, such as alpha-methylstyrene, chloromethyl styrene, and hydroxymethylstyrene, gamma-meta-KURIROSHIKI propyltrimethoxysilane, a 1-vinyl-2-pyrrolidone, etc. are mentioned.

[0021]In the case of what has carboxylic acid like an acrylic copolymer, especially binder resin may add an azole compound at a paste of this invention if needed. Carboxylic acid contained in an acrylic copolymer causes a metallic component and a reaction which are included in a magnetic body or a dielectric, and a viscosity rise of a paste and when severe, it may cause gelling. Acting as a rust-proofer is known for forming a tunic in the surfaces, such as copper, and by the same operation, the azole compound can prevent a reaction with metal and active groups, such as carboxylic acid of binder resin, and can control a viscosity rise and gelling. As an azole compound with such an operation, 1,2,3-benzotriazol, 1H-tetrazole, benzothiazole, etc. are raised.

[0022]A paste of this invention is obtained by mixing the above-mentioned structure uniformly, for example with kneading apparatus and dispersion devices, such as 3 roll mills and KOBORUMIRU. An example is raised and explained. After mixing an organic component uniformly thoroughly with a mixer or a stirrer, the end of conducting powder is added, and also it mixes, and preliminary distribution is performed. Then, it kneads through 3 roll mills. As for 3 roll mills, it is preferred to let it pass continuously 8 times from 2 times.

[0023]Next, although an example of formation of a dielectric layer or a magnetic layer using a paste by this invention is explained, this invention is not limited to this.

[0024]On an alumina substrate etc., by screen-stencil, a paste is applied and it dries. At 70 °C - 100 °C, from several minutes, it heats for 1 hour and dries. Then, it calcinates at an electric furnace, a belt furnace, etc., and decompose, and an organic component is volatilized and a dielectric film or a magnetic substance film can be formed by making inorganic powder sinter. Although they change with kinds of inorganic powder board contained, a firing environments and temperature are nitrogen atmospheres, hydrogen atmospheres, etc. containing atmospheric air, a nitrogen atmosphere, and 10-100 ppm of oxygen, at temperature of 500-1000 °C, are held for 1 to 60 minutes, and are calcinated.

[0025]Although a dielectric film formed with the paste of this invention and a magnetic substance film are used suitably for chips, such as a chip inductor and a chip capacitor, a module board, etc. which are mounted in a notebook computer or a cellular phone, they are not limited to these uses.

[0026]

[Example]Although the following examples explain this invention concretely, this invention does not receive any restriction according to these examples. The paste was adjusted in the way described below about each presentation shown in Table 1, and pattern processing nature was examined. The used raw materials are shown below.

[0027]

A. -- inorganic powder 1Dglass powder 50 mean particle diameter of 2 micrometers. Softening temperature 477 °C The specific gravity 5.2 glass powder 2. D50 mean particle diameter of 2 micrometers Softening temperature 398 °C. 3Dspecific gravity 5.0 glass-powder 50 mean particle diameter of 2 micrometers. Softening temperature 520 °C The specific gravity 4.9 glass powder 4. D50 mean particle diameter of 0.1 micrometer Softening temperature 477 °C. 5Dspecific gravity 5.2 glass-powder 50 mean particle diameter of 5 micrometers. Softening temperature 477 °C The specific gravity 5.2 ferrite powder 1. D50 mean-particle-diameter 0.4 micrometer nickel-Zn-Cu system . 2Dspecific gravity 5.3 ferrite-powder 50 mean-particle-diameter mNi-Zn-Cu system of 0.05micro Specific gravity 5.3 ferrite-powder 3 D50 mean-particle-diameter 2 micrometer nickel-Zn-Cu system 4Dspecific gravity 5.3 ferrite-powder 50 mean particle diameter of 0.4 micrometer. nickel-Zn system specific gravity 5.3 barium titanate D50 mean particle diameter of 0.7 micrometer Specific gravity 6.1.

[0028]B. Polymer acrylic polymer" JON krill "611 (product made from Johnson Polymer)

Methacrylic acid-methyl methacrylate copolymer oxidation 50 Weight average molecular weight 8,800 (in addition, the weight average molecular weight in an example and a comparative example was obtained by polystyrene conversion with gel permeation chromatography (GPC)).

[0029]C. Stabilizer 1,2,3-benzotriazol (made by Wako Pure Chem)

D. Leveling agent "DISUPARON"L1980 (made in Kusumoto Chemicals)

E. dispersing agent" NOPUKO -- sparse -- "092 (made by Sannopuko)

F. Solvent gamma-butyrolactone (made by Tonen Chemical).

[0030]A solvent is mixed with paste adjustment (1) polymer, and it heated for 3 hours and was made to dissolve at 60 °C.

(2) The polymer solution was cooled to the room temperature, all other presentations

were mixed, and it mixed with the motor uniformly thoroughly at the room temperature at 200 rpm for 30 minutes using churning feather.

(3) The obtained slurry was kneaded with 3 rolls (EXACT model 50), and the paste was obtained.

[0031]The printing (1) paste was completely applied by screen-stencil on the 96% alumina substrate of a 7.5-cm angle (made by Nikko Corp.). The screen used the SUS#325 mesh.

(2) The printed substrate was dried at 90 °C in hot wind oven for 30 minutes. There were 10 micrometers of thickness after desiccation.

[0032]Temperature up was carried out from a room temperature to 850 °C among atmospheric air in 2 hours using the calcination (1) electric furnace.

(2) It cooled naturally in the furnace after the maintenance for 10 minutes at 850 °C.

All results were shown in Table 1.

[0033]Examples 1-3 and the comparative examples 1 and 2 showed the softening temperature of glass powder, and the influence of particle diameter. Since the specific gravity of glass differs, weight distributions differ in each example, but in a volume fraction, Examples 1-6 and the comparative examples 1 and 2 are glass/ferrite = 38/62vol% altogether. Although the good result was altogether obtained by a degree of sintering, printing surface smoothness, electrical property, etc. in Example 1, after calcinating in order for glass to become soft before organic component evaporation since the softening temperature of glass is too low, and to wrap an organic component in the comparative example 1, the residue of the organic component remained, and the degree of sintering worsened. In the comparative example 2, since the softening temperature of glass was too high, sintering did not progress. In Examples 2 and 3, although the degree of sintering was good, since the diameter of a glass particle was too small, condensation occurred easily, and the diameter of a glass particle was too large and unevenness tends to have been possible in Example 3, by Example 2, printing surface smoothness all fell a little. Examples 4 and 5 show the influence of the particle diameter of ferrite powder with the same presentation as Example 1. Although the degree of sintering and the electrical property were good, even if the diameter of ferritic grain was too large and it was too small, printing surface smoothness printing surface smoothness fell. Example 6 is the same combination as Example 1, and changed ferrite powder into the nickel zinc system from the nickel zinc-copper system. The good result equivalent to Example 1 was obtained. Example 7 is a case where barium titanate which is a ferroelectric instead of a ferrite is used, and was made into glass/barium titanate = 38/62vol% like Examples 1-6 also in this case. Also in this case, the paste produced with the composition of this invention had a degree of sintering, an electrical property, and good printing surface smoothness. Examples 8 and 9 are examples which changed glass / ferrite ratio using the same raw material as Example 1. Glass / ferrite ratio = in Example 8 made into 25/75vol%, although an electrical property and printing surface smoothness did not have inferiority in Example 1, the degree of sintering fell. Glass / ferrite ratio = in Example 9 made into 50/50vol%, although a degree of sintering and printing surface smoothness were good, since there were few ferrite contents, the amplitude permeability of the film which calcinated the paste compared with Example 1 fell, and the electrical property fell.

[0034]Example 10 is an example at the time of removing 1,2,3-benzotriazol from Example 1. Although there was no problem in a degree of sintering, an electrical

property, and printing surface smoothness, the viscosity stability after a mothball fell from Example 1.

[0035]

[Table 1]

表 1	ガラス粉末	比重量	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	実施例 6	実施例 7	実施例 8	実施例 9	実施例 10
	ガラス粉末 1	5.2	26.3			26.3	26.3	26.3	23.1	17.3	34.7	26.3
	ガラス粉末 2	5.0	25.6									
	ガラス粉末 3	4.9		25.3								
	ガラス粉末 4	5.2			25.3							
	ガラス粉末 5	5.2			25.3							
磁性体粉末	フェライト粉末 1	5.3	43.7	44.4	43.7					52.7	35.3	43.7
	フェライト粉末 2	5.3				43.7						
	フェライト粉末 3	5.3					43.7					
	フェライト粉末 4	5.3						43.7				
誘電体粉末	チタン酸バリウム	6.1							46.9			
ポリマー	“ジョンクラリル” 611		30	30	30	30	30	30	30	30	30	30
溶剤	γ-ブチロラクトン		30	30	30	30	30	30	30	30	30	30
安定剤	1,2,3-ベンゾトリアゾール		7	7	7	7	7	7	7	7	7	0
分散剤	“ノゾコスバース” 092		0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
レベリング剤	“デイスバロン” LI980		0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
評価結果	850℃焼結性		○	×	×	○	○	○	○	○	○	○
	露光特性		○	×	×	○	○	○	○	○	○	○
	粘度安定性		○	○	○	○	○	○	○	○	○	○
	印刷平滑性		○	○	○	△	△	△	○	○	○	○

[0036]

[Effect of the Invention]In this invention, it has the above composition.

Therefore, the paste which can form the magnetic substance film or dielectric film of high performance after calcination below 1000 \*\* including magnetic substance powder or dielectric powder can be obtained.

[Translation done.]